

## METHOD 7471B

### MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

#### 1.0 SCOPE AND APPLICATION

1.1 Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

#### 2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

2.2 This method is a cold-vapor atomic absorption method and is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical instrument detection limit (IDL) for this method is 0.0002 mg/L.

#### 3.0 DEFINITIONS

Refer to Chapter One and Chapter Three for a listing of applicable definitions.

#### 4.0 INTERFERENCES

4.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/Kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/Kg had no effect on recovery of mercury from spiked samples.

4.3 Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 254 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate.

4.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

## 5.0 SAFETY

Refer to Chapter Three for a discussion on safety related references and issues.

## 6.0 EQUIPMENT AND SUPPLIES

6.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

6.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

6.3 Recording device: Any multirange variable-speed recorder compatible with the UV detection system or any other compatible data collection device.

6.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One inch diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

6.5 Air pump: Any peristaltic pump capable of delivering 1 L/min air may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

6.6 Flowmeter: Capable of measuring an air flow of 1 L/min.

6.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

6.8 Drying tube: 6-in. x 3/4-in. diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

6.9 The cold-vapor generator is assembled as shown in Figure 1 of reference 1 or according to the instrument manufacturers instructions. The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system. Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. Equal volumes of 0.1 M  $\text{KMnO}_4$  and 10%  $\text{H}_2\text{SO}_4$ , or
2. Iodine 0.25% in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barneby and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

6.10 Heating source - Adjustable and capable of maintaining a temperature of  $95 \pm 3^\circ\text{C}$ . (e.g., hot plate, block digester, microwave, etc.)

6.11 Graduated cylinder or equivalent volume measuring device.

## 7.0 REAGENTS AND STANDARDS

7.1 Reagent Water: Reagent water will be interference free. All references to water in this method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

7.2 Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated  $\text{HNO}_3$ .

7.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1 liter.

7.4 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. A 10% solution of stannous chloride can be substituted for stannous sulfate.

7.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

7.6 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

7.7 Mercury stock solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL (1.0 mL = 1.0 mg Hg).

7.8 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing  $0.1 \mu\text{g/mL}$ . This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before adding the aliquot.

## 8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

8.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

8.3 Non-aqueous samples shall be refrigerated, when possible, and analyzed "as soon as possible."

## 9.0 QUALITY CONTROL

Refer to Method 7000.

## 10.0 CALIBRATION AND STANDARDIZATION

10.1 Standard preparation: Transfer 0.0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles or equivalent. Add enough reagent water to each bottle to make a total volume of 10 mL. Add 5 mL of aqua regia and heat 2 min at  $95 \pm 3^\circ\text{C}$ . Allow the sample to cool; add 50 mL reagent water and 15 mL of  $\text{KMnO}_4$  solution to each bottle and heat again at  $95 \pm 3^\circ\text{C}$  for 30 min. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Section 11.3.

10.2 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart or other recording device and read the mercury value from the standard curve. Duplicates, spiked samples, and check standards should be routinely analyzed.

## 11.0 PROCEDURE

11.1 Sample preparation: Weigh a 0.5 - 0.6g aliquot of a well homogenized sample and place in the bottom of a BOD bottle or other appropriate analysis vessel. Add 5 mL of reagent water and 5 mL of aqua regia. Heat two minutes at  $95 \pm 3^\circ\text{C}$ . Cool; then add 50 mL reagent water and 15 mL potassium permanganate solution to each sample. Mix thoroughly, then heat for 30 min at  $95 \pm 3^\circ\text{C}$ . Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

CAUTION: Do this addition under a hood, as  $\text{Cl}_2$  could be evolved. Add 55 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under Section 11.3.

11.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 mL of concentrated  $\text{H}_2\text{SO}_4$  and 2 mL of concentrated  $\text{HNO}_3$  are added to the 0.5 - 0.6 g of sample. Add 5 mL of saturated  $\text{KMnO}_4$  solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at  $121 \pm 3^\circ\text{C}$  and 15 lb for 15 min. Cool, dilute to a volume of 100 mL with reagent water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under Section 11.3. Refer to the caution statement in Section 11.1 for the proper protocol in reducing the excess permanganate solution and adding stannous sulfate.

11.3 Analysis: At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 L/min, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 seconds. As soon as the absorbance reading levels off (approximately 1 minute), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the fritted tubing from the BOD bottle, and continue the aeration.

## 12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

## 13.0 METHOD PERFORMANCE

13.1 Precision and accuracy data are available in Method 245.5 of Methods for Chemical Analysis of Water and Wastes.

13.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

## 14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477.

## 15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

## 16.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.5.
2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

## 17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The pages to follow contain Table 1 and a flow diagram of the method procedure.

TABLE 1  
METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	Not known	12, 12 µg/g
Wastewater treatment sludge	Not known	0.4, 0.28 µg/g

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